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Thermally stimulated discharge currents in cellulose acetate

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Abstract : Depolarization current characteristics of solution grown cellulose acetate (CA) samples have been studied as a function of poling fields and heating rates. Thermally stimulated depolarization currents (TSDC) spectra of cellulose acetate, poled with different poling fields E_p s (= 2.8, 9.0) $\times 10^3$ volts/cm at a constant poling temperature T_p = 100°C using linear heating rate, β = 3 °C/min, consist of two well resolved peaks (located at 90 ± 1°C and 202 ± 2 °C) which are attributed to the molecular motion of the polar side groups and release of the remaining part of the frozen dipoles by their cooperative motion with adjoining segments of the main polymer chain. The TSDC thermograms of cellulose acetate samples poled with constant E_p (9.0 × 10^3 volts/cm) and T_p (100°C) for different β's (3, 5 and 7°C/min) are also characterized with two peaks located at around 90–155°C and 205–270°C, respectively. It has been observed that heating rate considerably affects the position and magnitude of currents of both the peaks.

Keywords : Thermally stimulated depolarization currents, cellulose acetate, dipolar polarization

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1. Introduction

The electret effect in polymers can be produced by the orientation of dipoles and/or trapping of charge carriers injected from the electrodes as well as generated in the bulk. Increase of the temperature of polymer electret, induces various transitions in them, resulting in increased molecular motions which cause detrapping of charge carriers from various levels. These transitions can be investigated by the thermally stimulated discharge current (TSDC) technique [1]. The TSDC technique is a simple but effective tool for

extracting information about internal structure and molecular relaxations, as well as the establishment and decay of space charge due to trapping of charge carriers and their subsequent thermal release from traps in polymers [2–5]. Various reports on TSDC behaviour of polymers and different relaxation processes contributing to the observed peaks in the corresponding thermograms are available [6–9]. However, the nature of various polarization processes and their relative contribution to the electret state of the polymer are not yet fully understood.

Synthetic high polymers of cellulosic materials are excellent electrical insulators. When they dry, contain large numbers of traps and exhibit structural deformations at certain transition temperature [10]. The cellulosic derivatives –C–O–C groups are built into the main polymer chain linearly and also in the form of a 6-membered glucopyranose ring with flexible polar side groups. The cellulose molecule is ribbon-like in form or, more explicitly, is a sequence of flat plates (the rings of atoms) linked together (by the oxygen bridges). At the oxygen bridge, bending out of the plane of the ribbon and twisting are fairly easy so that the molecule is quite flexible although much stiffer than a polyethylene chain. The hydroxyl (–OH) groups strongly attract other hydroxyl groups through the formation of hydrogen bonds. The knowledge of trap parameters and phase transition mechanisms is of the utmost importance in characterizing them for a specific use [11]. In this paper, TSDC studies of the cellulose acetate thermoelectret have been discussed specially by varying the heating rate.

2. Experimental

The isothermal immersion technique was utilized for preparing thin film of cellulose acetate. The solution was prepared in a glass beaker by dissolving 5.0 gm cellulose acetate in 100 ml of commercially pure chloroform. The solution was continuously stirred for 30 min by means of a teflon-coated magnetic stirrer. Therefore, it was stirred and heated to 60°C to yield a homogeneous solution. The glass beaker containing the solution was then immersed in a constant temperature oil bath. Ultrasonically cleaned, vacuum aluminized microscopic glass slides were immersed vertically into the solution for a period of about 20 min. After deposition of the film, the glass slide was taken out and dried in an oven at 70°C for 24 h. This was followed by room temperature outgassing at 10^{-5} torr for a further period of 24 h. The upper metal (Al) electrode was also vacuum deposited. The method of sample polarization was similar to that reported earlier [12]. The voltage was applied from a stabilized voltage unit (EC-4800D). The polarized samples were subsequently short-circuited for an arbitrary time of 15 min so as to remove any frictional and stray charges. The short circuit TSCs were then recorded by reheating the sample with a Keithley 600B electrometer which was grounded and shielded so as to avoid ground loops or extraneous noise. Infrared absorption spectra of cellulose acetate was taken at room temperature using infrared spectrophotometer model "Spectrometer 200 MOM". The ultraviolet absorption spectra of these films were taken using a double beam spectrometer "Pye-Unicam sp 700 A".

3. Results and discussion

The ultraviolet (UV) spectrum of cellulose acetate exhibits a shoulder at 225 nm alongwith an ill-defined band at 275 nm (Figure A). The infrared spectrum is characterized by the

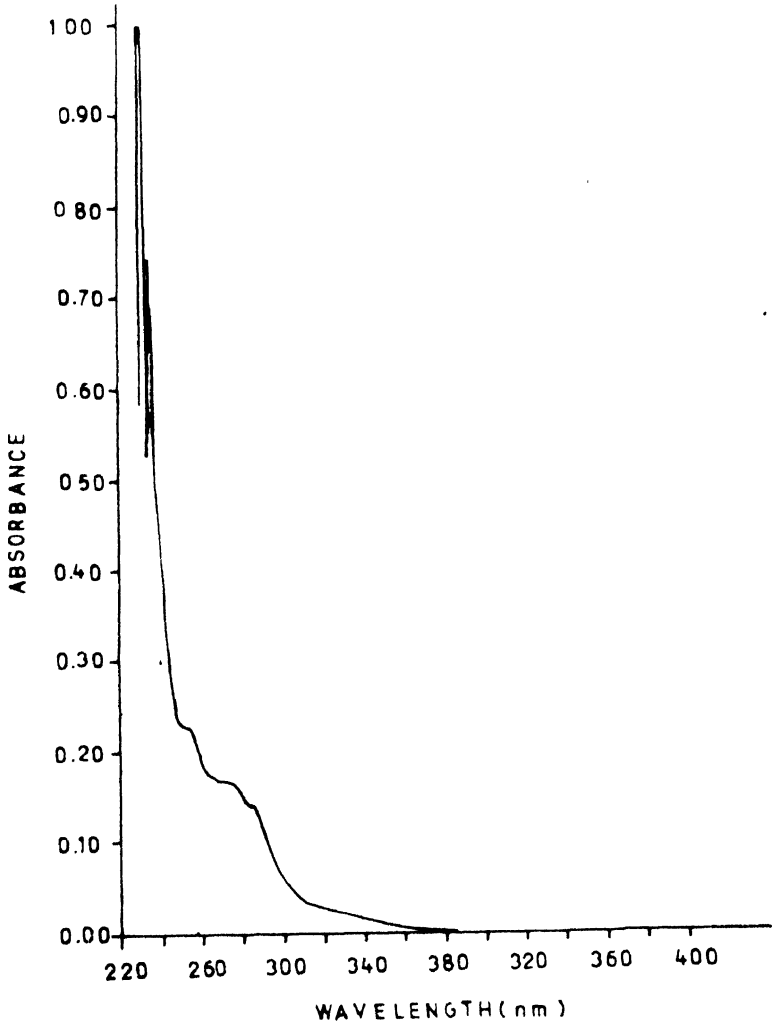

Figure A. Ultraviolet spectrum of cellulose acetate.

presence of four important bands: C=O stretching band at 1745 cm^{-1}; C–CH_3 deformation band at 1370 cm^{-1}; C–O at 1055 cm^{-1}. In addition to the above mentioned bands, the spectrum also contains a large number of ill defined/weak bands (Figure B).

Figure 1 shows the depolarization current characteristics of cellulose acetate samples polarized under identical conditions at polarizing temperatures (T_p) = 100°C for polarizing time (t_p) = 3.6×10^3 sec and with different polarizing fields (E_p's) using heating rate (β) = 3°C/min. In the figure, curves *A*, *B*, *C* and *D* correspond to polarizing fields of 2.8×10^3, 4.2×10^3, 7.2×10^3 and 9.0×10^3 volts/cm respectively. It is seen from the

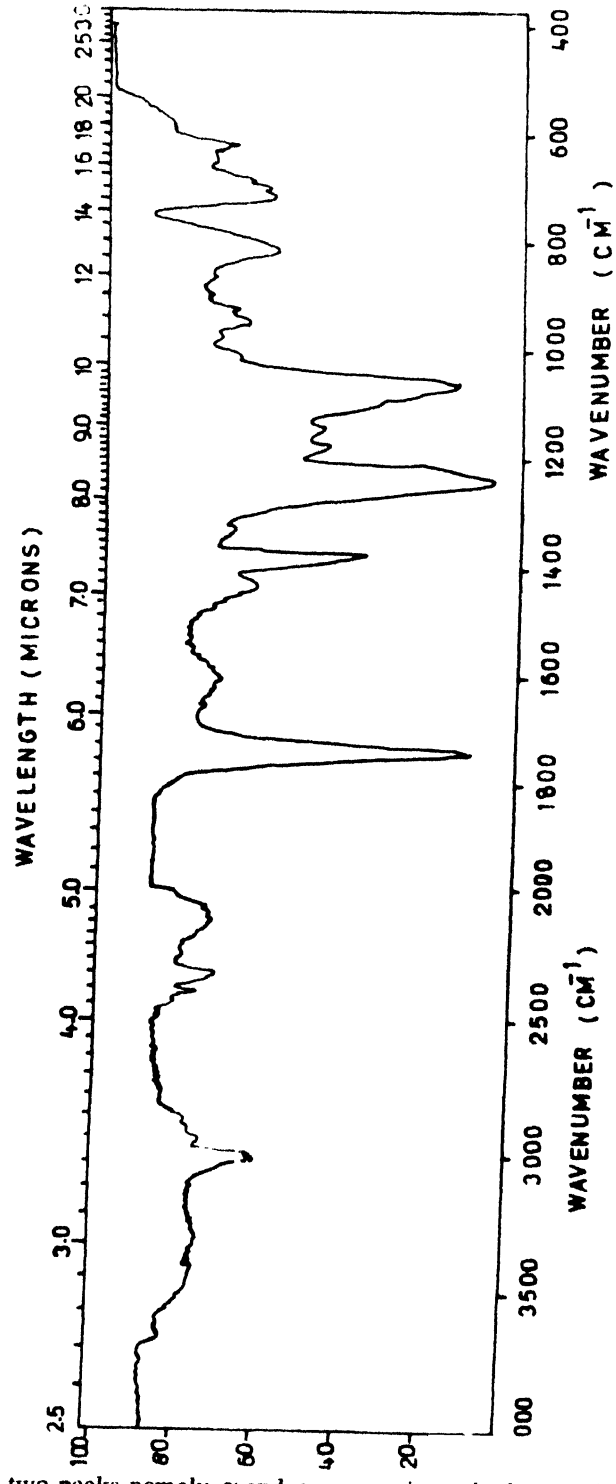

Figure A. Ultraviolet spectrum of cellulose acetate.

Figure 1, that two peaks namely α and ρ, appear in each characteristic in the ascending order of temperature. α-peak is observed to be centered around 90 ± 1°C and ρ-peak around 202 ± 2°C. With the increase in poling field, the position of peak temperature (T_m) of both

the peaks remains unchanged, whereas the magnitude of the peak current (I_m) of both the peaks increases.

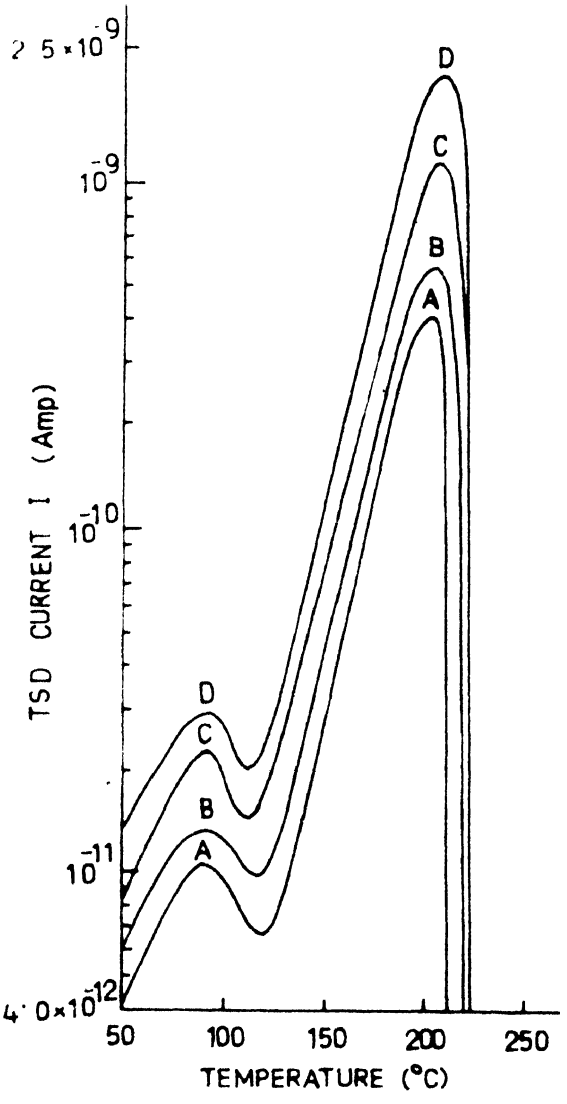

Figure 1. TSDC spectra of cellulose acetate samples at constant poling temperature (100 C) and heating rate 3 C/min with different poling fields (*i.e.* 2.8×10^3, 4.2×10^3, 7.2×10^3 and 9.0×10^3 volts/cm)

Charge released (Q) during the discharge was calculated by integrating the current *versus* temperature/time curves. Peak current and charge released *vs* poling fields plots for the α and ρ-peaks are shown in Figure 2. Peak current and released charge for α-peak show a linear rise with poling field up to 7.2×10^3 volts/cm, beyond which the rise becomes less than that which is expected for the linear relationship. However, the behaviour of peak current and release charge for ρ-peak is different. Both peak current and released charge show non-linear variation with poling field E_p in lower field region and they appear to be varying superlinearly in the higher field region. Initial rise plots for all the curves and peaks

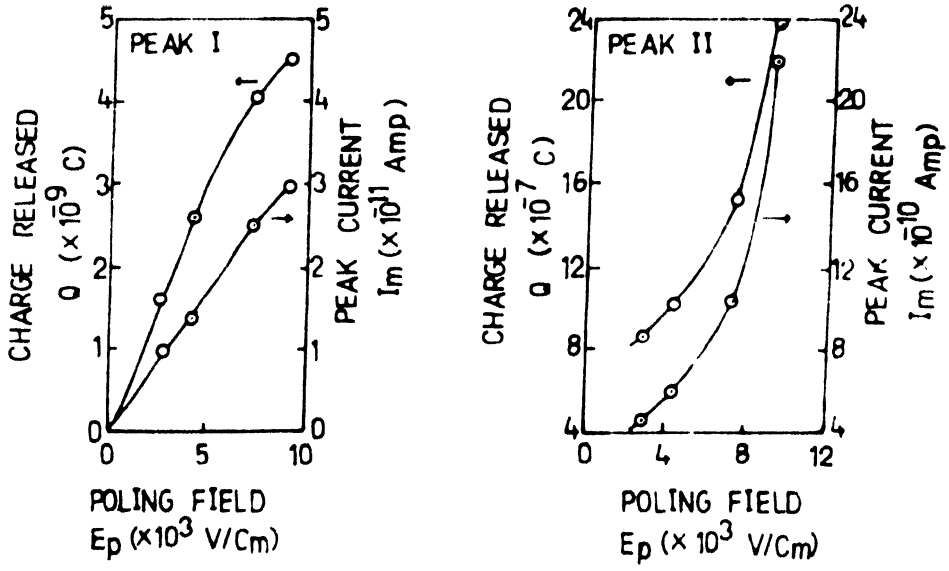

Figure 2. Plots of peak current (I_m) and released charge *versus* poling fields for α and ρ-peaks

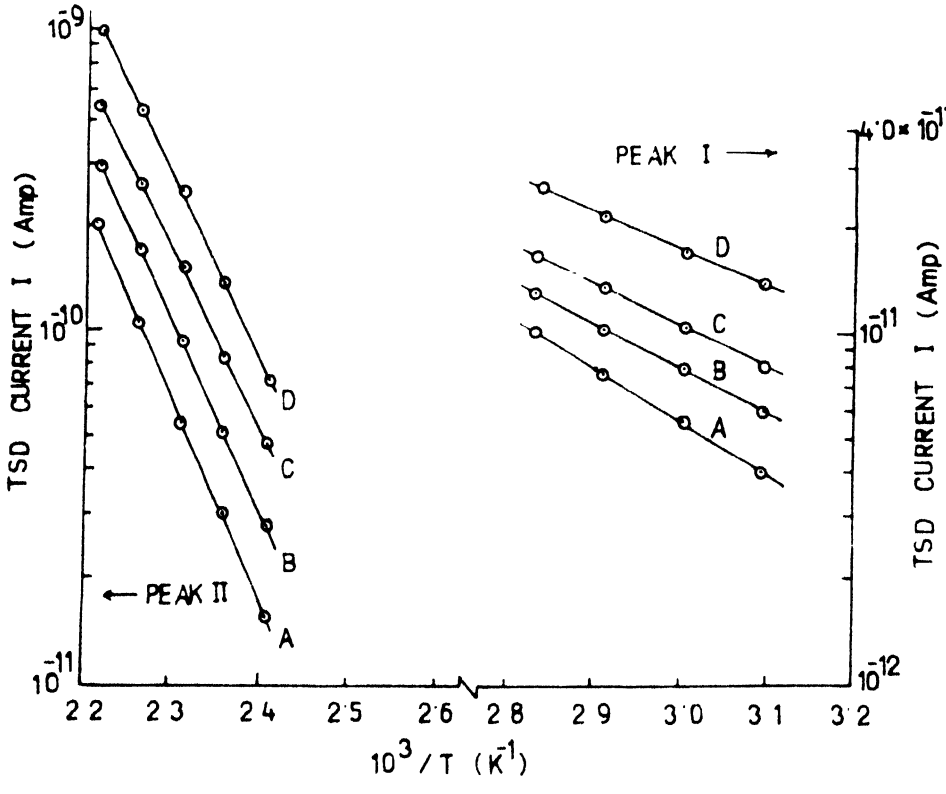

Figure 3. Initial rise plots of TSDC spectra of Figure 1

of Figure 1 are shown in Figure 3 and the activation energies have been calculated from the slope of these straight-line plots. The value of activation energy for α-peak decreases with the increase in E_p, while no variation of activation energy is found with the increase in E_p for ρ-peak.

To study the effect of heating rate (β) variation, the cellulose acetate samples were poled at different T_p's (60–110°C) with constant E_p (9.0×10^3 volts/cm). Excitation of TSD

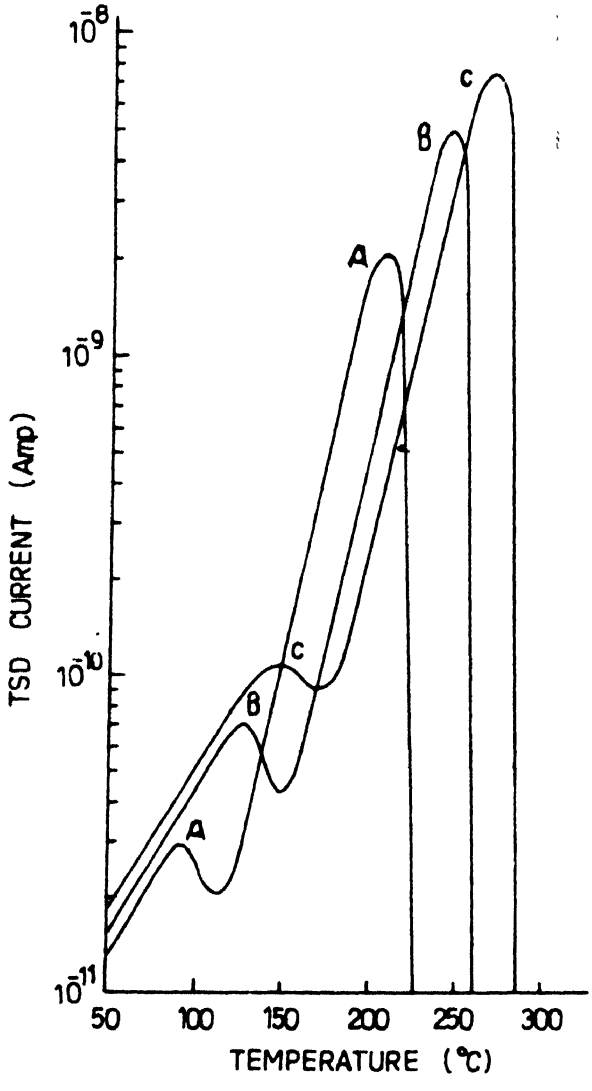

Figure 4. TSDC spectra of cellulose acetate samples poled at constant T_p (100°C) and poling field (9.0×10^3 volts/cm) with different heating rates (3, 5 and 7°C/min)

current in the temperature range (60–110°C) revealed that both the peaks diminished in intensity without any shift in peak position. A sort of saturation in intensity of the peak was

observed when the samples were poled above 100°C (result not shown). That is why the effect of heating rate was investigated by poling the samples at 100°C with poling field 9.0×10^3 volts/cm. Figure 4 exhibits TSDC spectra of cellulose acetate samples at constant T_p (100°C) and E_p = (9.0×10^3 volts/cm) with different β's = (*i.e.* 3, 5 and 7°C/min). Increase in β has an effect of increasing the magnitude of current peaks and shifting them to a higher temperature. The peaks are broadened with increasing β, but the broadening in ρ-peaks is more pronounced than in the α-peak. Peak temperature (T_m) and peak current (I_m) at various heating rates are listed in Table 1.

Table 1. Effect of heating rate on peak temperature and peak current.

Heating rate (β) (°C/min)	Peak temperature (°C), T_m		Peak current (I_m)	
	α-peak	ρ-peak	α-peak	ρ-peak
3	90	205	3.0×10^{-11}	2.2×10^{-9}
5	125	240	7.2×10^{-11}	5.2×10^{-9}
7	150	265	1.1×10^{-10}	8.0×10^{-9}

It is obvious from Table 1 that current maxima vary almost proportionally with the heating rate. Garlick and Gibson's [13] initial rise plots (log current *versus* $10^3/T$) of α and ρ peaks are shown in Figure 5. The close parallelism of initial rise plots suggests that the initial slope of the current is not altered due to change of heating rate. Activation energy values 0.26, 0.24 and 0.25 eV of α-peak and 0.97, 0.98 and 1.04 eV for ρ-peak at 3, 5 and 7°C/min respectively are not significantly different within experimental limits. Modified plot using the method of Bucci and Freschi [14] *i.e.* log of remaining charge on the film divided by the current at temperature *vs* the reciprocal of that temperature has been shown in Figure 5 for the α-peak of curve A of Figure 1.

The value of activation energy from the modified plot comes out to be 0.26 eV which is in fair agreement with the value calculated from initial rise method. The analysis was also applied for the ρ-peak but the modified plot did not turn out to be of single slope.

Natural relaxation time τ_0 and the peak temperature T_m are related through the relation

$$\tau_0 H \exp \frac{H}{kT_m} \quad \frac{kT_n}{\beta} \tag{1}$$

or,

$$\frac{\beta}{T_m^2} = \overline{H}\tau_0 \exp\left|-\frac{H}{kT_m}\right. \tag{2}$$

Therefore,

$$\log\left(\beta/T_m^2\right) = \text{Constant}\left(-\frac{H}{kT_m}\right) \tag{3}$$

where k is the Boltzmann's constant and H is the activation energy. According to eq. (3), H can be calculated by plotting $\log(\beta/T_m^2)$ *vs* $10^3/T_m$. These plots for α and ρ-peaks are

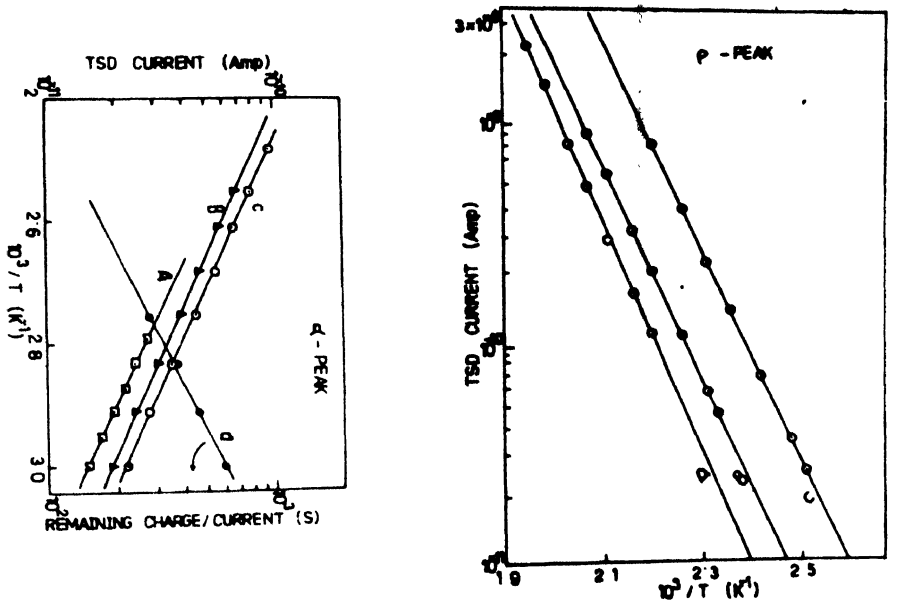

Figure 5. Initial rise plots for α and ρ-peaks of TSDC spectra of Figure 1. Curve D is the modified plot corresponding to the α-peak of Curve A of Figure 1.

shown in Figure 6. Activation energy of α-peak is determined to be 0.23 eV which is in agreement with the value calculated from initial rise or modified plot. Activation energy of ρ-peak is evaluated to be 0.42 eV which is much less than the value calculated from initial rise method.

Under the influence of electric field, the irregularly distributed dipoles of side chains are mobilized/oriented in a certain direction. Thermal activation at a constant rate causes the release of charges due to their mobilization giving a peak at the rate of maximum release of charge [15]. The origin of TSD currents can be attributed to the following mechanisms [16,17] : (i) polarization due to polar side group/dipole alignments; (ii) ions trapped in defects on dislocations in crystalline region; (iii) space charge built up due to migration of ions over microscopic distance, and (iv) the space charge injected from the electrodes. The first two processes give a uniform volume polarization with heterocharge and the third process gives non-uniform homocharge or heterocharge depending upon the

electrode-dielectric work function while the fourth process is related to non-uniform homocharges only due to injected charge carriers from electrodes.

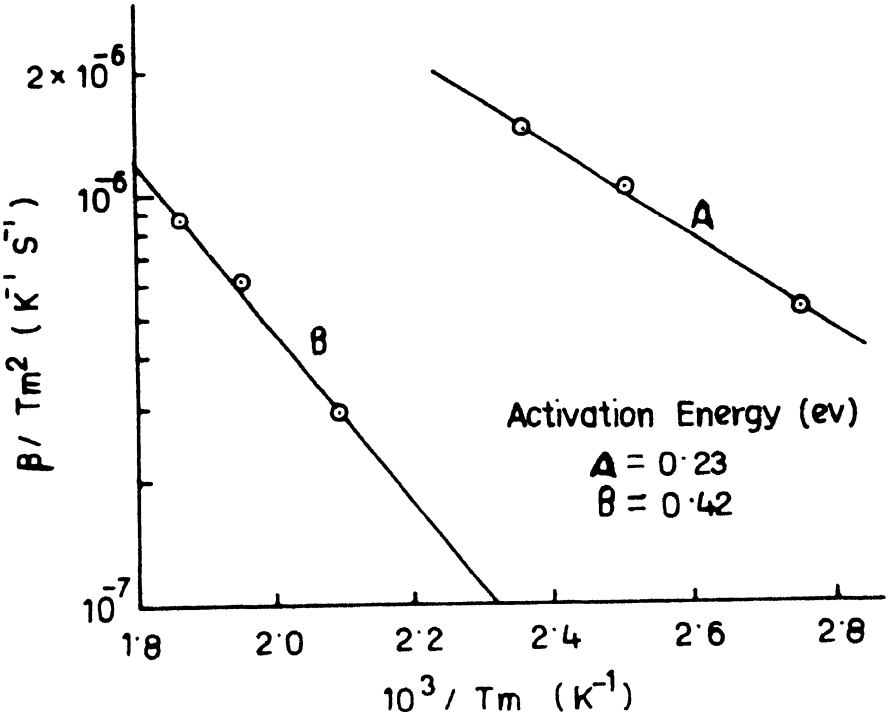

Figure 6. Log β/T_m^2 *versus* $10^3/T_m$. Plots A and B corresponds to α and ρ peak respectively

The value of activation energy 0.25 ± 0.04 eV associated with α-peak observed at 90 ± 1°C may correspond to molecular motion of the side groups. A decrease in activation energy 0.28 to 0.21 eV is observed with the increase in polarizing field from 2.8×10^5 to 9.0×10^5 volts /cm. This suggests that this peak is not due to a discrete level having a single relaxation but is a complex one having distributed activation energies. The peak current *versus* poling field and released charge *versus* poling field plots associated with α-peak are linear which suggests that the peak is of dipolar nature and this can be attributed to the relaxation of the polar acetate groups.

The superlinear behaviour of peak current *versus* poling field plot for ρ-peak (Figure 3) in the higher field region indicates the space charge phenomenon. The ρ-peak is not only due to single relaxation but seems to be more complex and may arise due to the release of the remaining part of the frozen dipoles by their cooperative motion with adjoining segments of the main polymer chains. The super linear increase of peak current and release charge *versus* poling field in the higher field region suggest that the second peak is contributed, both by electronic and ionic processes arising in the bulk and injected from

the electrodes which are subjected to a higher field. It is not a simple process but a complicated one of Maxwell-Wagner type.

Linearity of modified plot (Figure 5) suggests a uniform process to be operative. Equality of the values of activation energy calculated from initial rise, modified plot and according to eq. (3) further confirms uniform dipole polarization.

Origin of ρ-peak seems to be more complex because its modified plot (results not shown) is not observed to have a single slope. The activation energy of ρ-peak calculated from eq. (3) is only 0.42 eV as against the initial rise value ≅1 eV. Moreover, the dipolar contribution calculated from Debye's equation does not correspond to the high value of charge released. To account for the charge released probably the microscopic displacement of charges during polarization with their subsequent trapping may be held responsible.

The magnitude of peak currents increases with heating rate correspondingly. This is so because when heating is higher, the same charge has to be released in a shorter time. It is only the initial slope proportional to $1/\tau_0 \exp(-H/kT)$ which remains the same. Current maximas vary almost proportionally to the heating rate. At the same time they shift to a higher temperature because the polymer responds less quickly to a higher heating rate [18]. This may also be due to the combined effect of plastification [15,19] due to moisture content and rotation of polar acetate groups on account of different heating rates on thermal induction.

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